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Parametric Study of $\text{NCl}(a^1\Delta)$, $\text{NCl}(b^1\Sigma)$ from the reaction of $\text{Cl}/\text{Cl}_2/\text{He} + \text{HN}_3/\text{He}$

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ABSTRACT

By means of Microwave generator chlorine diluted by helium is dissociated to chlorine atoms that subsequently react with hydrogen azide to produce excited states of $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$. In this paper, the intensity of $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$ emission dependent on the flow rates of different gases is studied. Moreover, the production of $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$ along the reaction tube is also investigated. By using a simple titration method, we obtain the dissociation efficiency of molecular chlorine up to 100% at the flow rates of chlorine no more than 1mmol/s. We also achieve the quenching rate of $\text{NCl}(a^1\Delta)$ by Cl_2 is about $4 \times 10^{-13} \text{ cm}^3/\text{sec-molec}$ with excess flow rates of chlorine. Finally, the optimum parameters for $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$ production are summarized.

Key words: $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$, $\text{Cl}/\text{Cl}_2/\text{He} + \text{HN}_3/\text{He}$

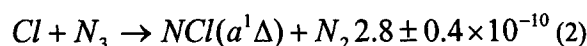
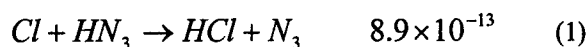
1. INTRODUCTION

Being the shortest wavelength chemical laser and the only laser based on electronic transition, the chemical oxygen-iodine laser (COIL) is of great interest owing to its potential applications in both industrial and military fields^[1]. As the energy source of the laser, $\text{O}_2(a^1\Delta)$ is produced by the reaction of gaseous chlorine with liquid basic hydrogen peroxide (BHP) in the singlet oxygen generator (SOG) which is a main part of the COIL and occupy the most of COIL in size and weight, so power-volume or power-weight efficiency is limited by the gaseous-liquid reaction. Moreover, there are the strong quenchers for excited atomic iodine, for example, water vapor and hydrogen peroxide produced in singlet oxygen generator (SOG). Consequently, it is necessary to look for metastable particles instead of $\text{O}_2(a^1\Delta)$ to pump iodine atoms.

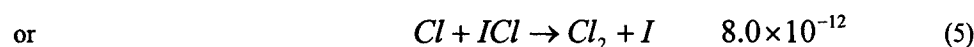
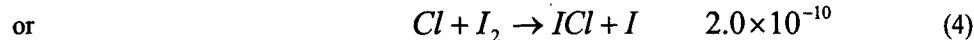
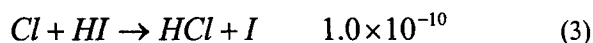
Bower and Yang^[2] reported the nearly resonant energy transfer from metastable $\text{NCl}(a^1\Delta)$ to atomic iodine in 1990 and obtained the reactive rate of $>1 \times 10^{-10} \text{ cm}^3/\text{s}$ which is much faster than that of $\text{O}_2(a^1\Delta)$ to atomic iodine. The concept of $\text{NCl}(a^1\Delta)/\text{I}$ as a newly possible laser system is becoming a hot point. Many papers^[3-7] about $\text{NCl}(a^1\Delta)$ energy transfer and quenching kinetics were reported. T.L.Henshaw^[8] and his group at Air Force Research Laboratory measured the gain on the 1315nm transition of atomic iodine in a subsonic flow of chemically generated $\text{NCl}(a^1\Delta)$ in 1999 and subsequently showed an output power of 180mW from a new energy transfer chemical iodine laser pumped by $\text{NCl}(a^1\Delta)$ at 1315nm in 2000^[9].

The mechanism of the system for a chemical atomic iodine laser pumped by $\text{NCl}(a^1\Delta)$ is general as following:

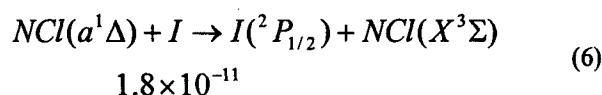
Production of $\text{NCl}(a^1\Delta)$



Production of atomic iodine

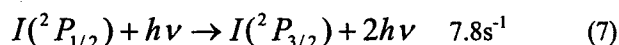


Production of excited atomic iodine

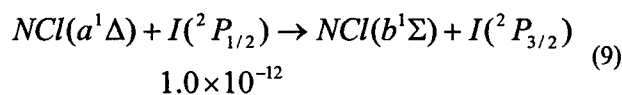
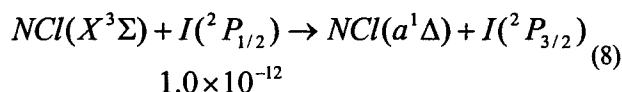


The above reactive rates are in units of $\text{cm}^3/\text{sec molec.}$

Lasing



In addition, there is a sharp increase of $\text{NCl}(b^1\Sigma)$ emission upon iodine being injected into the system of $\text{NCl}(a^1\Delta)/\text{Cl}/\text{He}/\text{Cl}_2/\text{HN}_3$, that is, a potential chemical laser at visible^[10] is based on



In this paper, the intensity of $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$ emission dependent on the flow rates of different gases was studied. Moreover, the production of $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$ along the reaction tube was also investigated. The results were presented and discussed and the quenching rate of $\text{NCl}(a^1\Delta)$ by Cl_2 is obtained. The optimum parameters for $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$ production were given finally.

2. EXPERIMENTAL

The diagram of the setup we used was shown in Figure 1. The reaction tube that was made of silica glass and had a length of 1.2m, the Microwave generator of 1000W, the gas supply system, OMA4 and the pumping system were indicated. The mixture of chlorine measured by a flow meter and helium measured by a flow meter flowed through the MW generator to produce chlorine atoms that then mixed and reacted with the mixture of hydrogen azide and helium at the ratio of 1:10. The chlorine and helium we used have a purity of 99.99%. HN_3 was produced by the method described in reference [2] and stored in an 180L steel container in which helium was input till the ratio of

He/HN₃ at 10:1. The pressure of the reaction tube was about 10 Torr and the linear velocity of the gases in the tube was around 100m/s. NCl(a¹Δ) and NCl(b¹Σ) emission was collected by OMA4 and processed by a computer.

3. RESULTS AND DISCUSSION

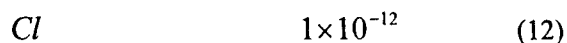
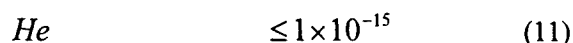
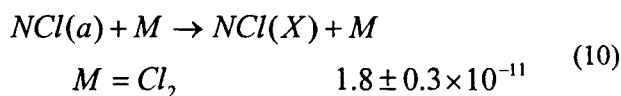
3.1 Spectrum of NCl(a¹Δ) and NCl(b¹Σ) emission

Upon HN₃/He being injected into Cl/Cl₂/He, the red fluorescence can be seen immediately. Spectra of NCl(a¹Δ) and NCl(b¹Σ) emission recorded by OMA4 are shown in Figure 2. The peaks of NCl(a¹Δ) emission around 1077nm and NCl(b¹Σ) emission around 665nm are the same with the results in the reference [11].

The OMA4 was calibrated by a standard tungsten lamp at 665nm and 1077nm and the coefficients were $5.73 \times 10^7 \text{ s}^{-1} \text{ Counts}^{-1}$ and $2.99 \times 10^8 \text{ s}^{-1} \text{ Counts}^{-1}$, respectively. By means of Einstein emission coefficients, the solid angle and the collected volume, we obtained that the densities of NCl(a¹Δ) and NCl(b¹Σ) at the experimental parameters were in the range of $10^{10-11} \text{ cm}^{-3}$ and 10^{7-8} cm^{-3} , respectively. The ratio of densities of NCl(a¹Δ) and NCl(b¹Σ) was about 10^{3-4} which is well accordant with the results of 6500 in reference [10]. However, it is the fact that the intensity counts of NCl(b¹Σ) emission looks like much stronger than that of NCl(a¹Δ) emission (reference Figure2). This is completely due to that the Einstein emission coefficient of NCl(b¹Σ) is much larger than that of NCl(a¹Δ) and the sensitivity of OMA4 is more sensitive at visible than IR range.

3.2 NCl(a¹Δ) and NCl(b¹Σ) emission along the reaction tube

The intensity of NCl(a¹Δ) and NCl(b¹Σ) emission along the reaction tube is shown in Figure 3. It can be seen that there is a maximum at the range of 4-5cm along the reaction tube at the experimental conditions of the helium flow rate of 19.7SLM, chlorine of 0.42SLM, HN₃/He mixture of 1.6SLM and the pressure of the reactor at 10Torr. This is easily understood because the production of NCl(a¹Δ) and NCl(b¹Σ) increases with the mixing which is better and better with the distance and on the other hand the quantity of NCl(a¹Δ) and NCl(b¹Σ) decreases with the distance owing to the quenching by many particles, for example, NCl(a¹Δ) quenched by the following particles.



Considering reaction formulas of (1), (10), (11), (12) and denoting [Cl₂], [He], [Cl] as [M], we can obtained the following kinetics equation,

$$\begin{aligned} \frac{d[\text{NCl}(a^1\Delta)]}{dt} &= k_1[\text{Cl}][\text{HN}_3] \\ &\quad - \Sigma k_m[M][\text{NCl}(a^1\Delta)] \end{aligned} \quad (13)$$

Input the linear velocity of the gas (denoted as u), the equation can be written as a function of the distance

(denoted as x),

$$\frac{d[NCl(a^1\Delta)]}{dx} = \frac{1}{u} \{k_1[Cl][HN_3] - \Sigma k_m[M][NCl(a^1\Delta)]\} \quad (14)$$

Assuming $[HN_3]$, $[M]$ and the reactive rates of k_1 and k_m as constants, and integrating the above equation as follows,

$$[NCl(a^1\Delta)] = \frac{A}{B} \cdot (1 - e^{-Bx}) \quad (15)$$

$$\text{Where, } A = \frac{1}{u} (k_1[HN_3]_0[Cl]), \quad B = \frac{1}{u} (\Sigma k_m[M])$$

If only considering the dominant reaction step (1), we can obtain that $[Cl]$ goes down with the distance according to the reaction kinetics equation,

$$\frac{d[Cl]}{dx} = -\frac{1}{u} \{k_1[Cl][HN_3]\}$$

So,

$$[Cl] = [Cl]_0 e^{-cx} \quad (16)$$

$$\text{Where } c = \frac{1}{u} k_1[HN_3]_0$$

So equation (15) becomes

$$[NCl(a^1\Delta)] = \frac{A_0}{B} \cdot e^{-cx} \cdot (1 - e^{-Bx}) \quad (17)$$

$$\text{Where } A_0 = \frac{1}{u} (k_1[HN_3]_0[Cl]_0)$$

The maximum of $NCl(a^1\Delta)$ along the distance can be easily obtained based on making the differential equation of formula (17) equal zero.

Also, both profiles have almost the same trend and the emission of $NCl(a^1\Delta)$ and $NCl(b^1\Sigma)$ spreads all over the tube inside according to spectrum measurements as well as sights. In the following we studied the relationship of intensity of $NCl(b^1\Sigma)$ emission and parameters of gaseous flow rates since $NCl(a^1\Delta)$ has the same trend with $NCl(b^1\Sigma)$ and the OMA4 has a higher signal-noise ratio at the visible.

3.3 $NCl(a^1\Delta)$ and $NCl(b^1\Sigma)$ emission dependent on ratio of He and Cl_2

The intensity of $NCl(b^1\Sigma)$ emission dependent on the ratios of He and Cl_2 was studied at the position of 5cm and indicated in Figure 4. The ratio of He and Cl_2 was changed by adjusting the flow rates of chlorine at a fixed flow rate of helium. The intensity of $NCl(b^1\Sigma)$ emission is almost completely stronger at the ratios of He and Cl_2 more than 30:1 in several flow rates of helium cases. In more detail, it also can be seen that the ratio of He and Cl_2 for the maximum intensity of $NCl(b^1\Sigma)$ emission increases with the flow rates of He. Even so, the ratio of helium and

chlorine at 30 is enough to protect atomic chlorine since it is not easy to charge for more diluent helium by means of the microwave generator.

3.4 NCl(a¹Δ) and NCl(b¹Σ) emission dependent on Cl₂

The intensity of NCl(b¹Σ) emission dependent on the flow rates of Cl₂ is shown in Figure 5 in which the maximum intensity of NCl(b¹Σ) emission was in the range of 0.25—0.4SLM for the flow rate of chlorine. More or less chlorine can cause to decrease the production of NCl(a¹Δ) and NCl(b¹Σ) because less chlorine only produces less chlorine atoms and consequently produces less excited particles, in contrast, excessive chlorine can quench the excited particles of NCl(a¹Δ) and NCl(b¹Σ). The relationship of the density of NCl(a¹Δ) and the density of Cl₂ is display in Figure 6. Now we only consider the quenching by Cl₂ since k_{He} is much less than k_{Cl_2} and the atomic chlorine is much less, the kinetics equation can be written as,

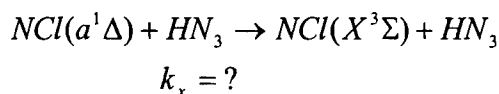
$$\frac{d[NCl(a^1\Delta)]}{dx} = \frac{1}{u}(-k_{Cl_2}[Cl_2][NCl(a^1\Delta)])$$

$$[NCl(a^1\Delta)] = [NCl(a^1\Delta)]_0 \cdot e^{-\frac{1}{u}k_{Cl_2}x} \quad (18)$$

Fitting the experimental data in Figure 6, the exponential coefficient of $\frac{1}{u}k_{Cl_2}x$ is simulated as 2×10^{-16} . Based on the linear velocity of ca. 10000cm/s and the collecting position of 5cm, the quenching rate of NCl(a¹Δ) by chlorine (denoted as k_{Cl_2}) is around 4×10^{-13} cm³/sec molec which is in good agreement with the result in reference [4].

3.5 NCl(a¹Δ) and NCl(b¹Σ) emission dependent on HN₃/He

The intensity of NCl(b¹Σ) emission dependent on the flow rate of HN₃/He at different flow rates of helium and chlorine is shown in Figure 7 in which it can be seen that the maximum NCl(b¹Σ) was produced at the flow rate of 2.5—3.5SLM of HN₃/He. Excess or less HN₃/He can cause the decrease of the production of NCl(a¹Δ) and NCl(b¹Σ) because less hydrogen azide only produces limited excited particles and extra hydrogen azide similarly quench the excited particles of NCl(a¹Δ) and NCl(b¹Σ) though the reaction rate of NCl(a¹Δ) quenched by HN₃ is unknown to us so far.



$$\frac{d[NCl(a^1\Delta)]}{dt} = k_1[Cl][HN_3] -$$

$$k_x[HN_3][NCl(a^1\Delta)] + k_m[M][NCl(a^1\Delta)]$$

Recently, we have done a series of experiments about changing the ratios of hydrogen azide over chlorine in another reactive device, the results are shown in Figure 8. If assuming the mixing efficiency is unity, we can obtain that the dissociation efficiency of chlorine based on the maximum flow rate of hydrogen azide,

$$\eta_{diss} = \frac{[HN_3]_{\max}}{[Cl_2]}$$

is 60%~100%

In summary, the optimum operating parameters for the present setup are listed in Table 1.

4. CONCLUSION

Through the parametric study of $NCl(a^1\Delta)$ and $NCl(b^1\Sigma)$ emission, it can be seen that the branch ratio of $NCl(a^1\Delta)$ and $NCl(b^1\Sigma)$ is about 10^{3-4} in the reaction system of $Cl/Cl_2/He + HN_3/He$. The ratio of helium and chlorine about 30 is enough to protect atomic chlorine since it is not easy to charge for more diluent helium by means of the microwave generator. Also, we obtained that the optimum parameters for the production of $NCl(a^1\Delta)$ and $NCl(b^1\Sigma)$ were the flow rates of chlorine in the range of 0.25—0.4SLM, hydrogen azide in the range of 0.25—0.35SLM, helium in the range of 11—14SLM and the pressure of the reaction tube at about 10Torr in our presently experimental conditions. More, the quenching rate of $NCl(a^1\Delta)$ by Cl_2 is about 4×10^{-13} cm³/sec molec. The dissociation efficiency of molecular chlorine can be up to 100% at the flow rates of chlorine no more than 1mmol/s.

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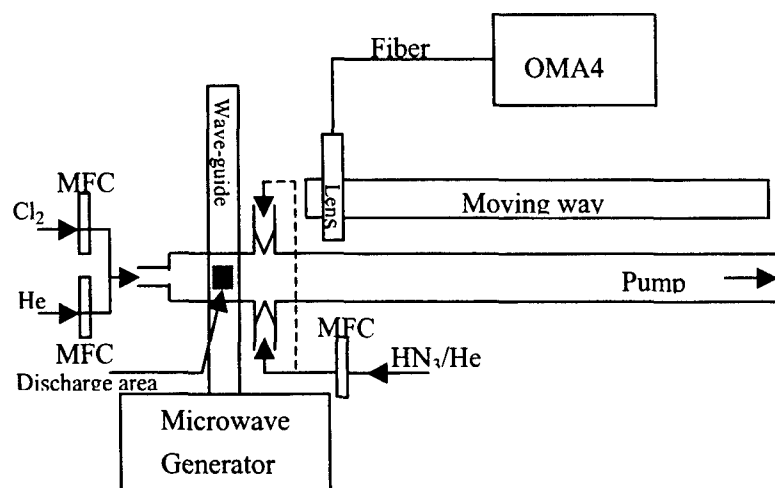


Figure 1 The schematic of the experimental setup

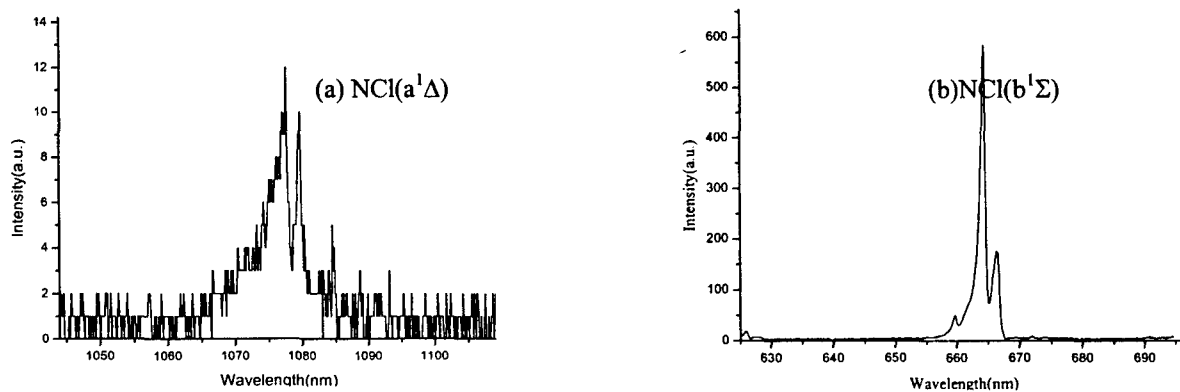


Figure 2 Spectra of $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$ emission

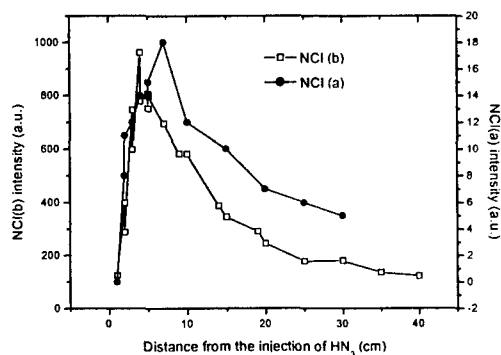


Figure 3 The intensity of $\text{NCl}(a^1\Delta)$ and $\text{NCl}(b^1\Sigma)$ emission along the reaction tube

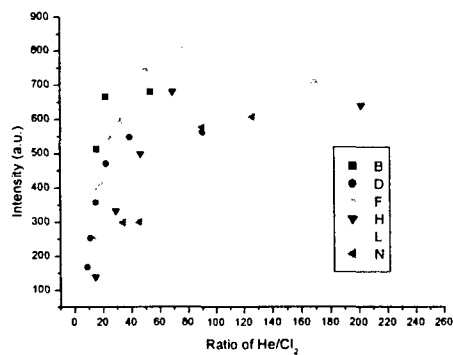


Figure 4 The intensity of $\text{NCl}(b^1\Sigma)$ emission dependent on the ratios of He and Cl_2 ,

B: He:4.8SLM; $\text{HN}_3/\text{He}(1:10)$:0.5SLM; D:He:8.1SLM; $\text{HN}_3/\text{He}(1:10)$:1SLM;
F: He:18.6SLM; $\text{HN}_3/\text{He}(1:10)$:2.5SLM; H: He:24.2SLM; $\text{HN}_3/\text{He}(1:10)$:1SLM;
L: He:30SLM; $\text{HN}_3/\text{He}(1:10)$:1SLM; N: He:39.2SLM; $\text{HN}_3/\text{He}(1:10)$:2SLM

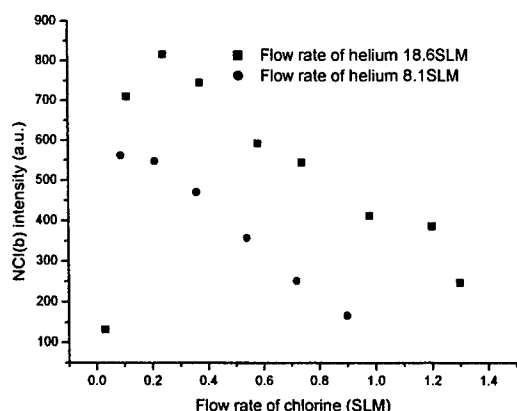


Figure 5 The intensity of $\text{NCl}(b^1\Sigma)$ emission dependent on the flow rates of Cl_2

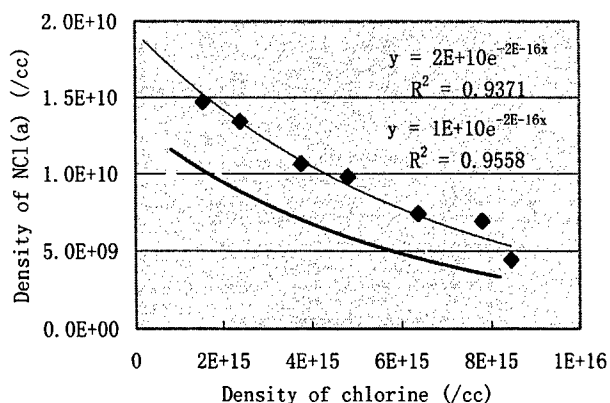


Figure 6 The dependence of density of $\text{NCl}(a^1\Delta)$ on the density of Cl_2

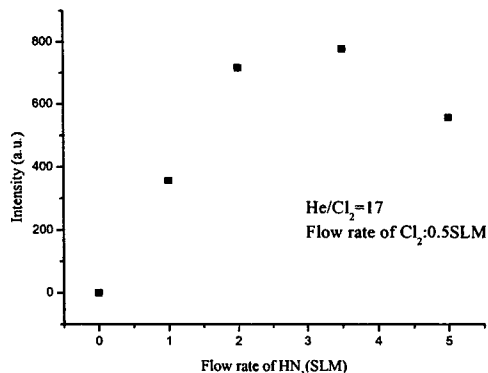


Figure 7 The intensity of $\text{NCl}(b^1\Sigma)$ emission dependent on the flow rate of HN_3/He

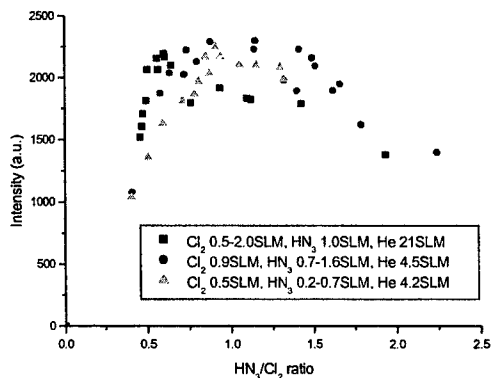


Figure 8 The relationship of the emission intensity of $\text{NCl}(b^1\Sigma)$ and the ratio of HN_3/Cl_2

Table 1 the optimum operating parameters for the present setup

HN_3 flow rate (SLM)	0.25—0.35
Cl_2 flow rate (SLM)	0.25—0.4
He flow rate (SLM)	11—14
Pressure (Pa)	1330
Diameter of the tube (cm)	2
Cl_2 dissociation efficiency (%)	60—100
Linear velocity (m/s)	100